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Corrections for Contamination Background in AMS ^{14}C Measurements[†]

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Abstract

Measurements of $^{14}\text{C}/^{13}\text{C}$ ratios were made on samples of Oxalic Acid and ^{14}C “dead” materials spanning the mass range from 10 μg to ~ 1 mg. These measurements have allowed the determination of both the amount, and the ^{14}C content, of the contaminant carbon introduced during sample processing in our laboratory. These data were used to correct measured $^{14}\text{C}/^{13}\text{C}$ ratios obtained from ANU Sucrose and “ \sim one-half-life old” test samples for the influence of the contaminant. The test samples spanned the 10 μg to ~ 1 mg mass range and the corrections were made using three different formulae. The results obtained from these calculations allow the accuracy of these background correction formulae to be evaluated.

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Introduction

In several studies, researchers have found that background levels in their AMS ^{14}C measurements rise with decreasing sample size and are consistent with the introduction of a constant mass of modern carbon during sample processing and/or measurement [1–3]. Several formulations have been developed to try to correct for the contaminant contribution to the measured ratios of unknown samples [e.g., 4–7].

In a recent study [6, 7], the accuracy of these formulations was tested through calculations which applied the various formulae to simulated samples derived from the two-component mixing of a model contaminant (of a given mass and ^{14}C content) with model (uncontaminated) unknown, standard or background materials. The results from these calculations indicated that several of the formulations suffered from significant inaccuracies under some conditions. In this study we have measured $^{14}\text{C}/^{13}\text{C}$ ratios for several sample materials to test the accuracy of three background correction formulations when applied to measurements obtained under our routine measurement conditions at CAMS.

The three formulations we have tested are from: 1) Donahue *et al.* [5] (which has been in the published literature for several years and is perhaps the most widely used), 2) Brown [6] and Brown *et al.* [7] (the only formulation in the model tests mentioned above that corrected accurately under all tested conditions), and 3) the traditional “subtraction ratio” formulation (a very simple equation which only corrected accurately in the model tests when ratios from unknown samples were normalized to ratios from standard samples of the same mass). The specific formulae used will be discussed below.

Measurements of Oxalic Acid and Background (“ ^{14}C free”) samples

The $^{14}\text{C}/^{13}\text{C}$ ratios of Oxalic Acid Standard (OX1) and “ ^{14}C -free” background samples were measured for samples spanning the mass range 10 μg to ~1 mg. The $^{14}\text{C}/^{13}\text{C}$ ratio of each sample was determined 3–6 times to 1% precision (10 000 counts), each of these determinations was normalized to the average of the ratios obtained for four nearby ~1 mg OX1 samples, and then the normalized ratios were averaged to yield the final normalized ratio for the sample. For many of the samples containing less than ~30 μg , only one or two determinations could be made before the ion current dropped to unacceptable levels.

The normalized ratios obtained for the OX1 samples are shown in Figure 1. The decrease in the normalized ratios with decreasing sample mass can be attributed to the addition of contaminant carbon whose ^{14}C content is lower than that of the OX1 Standard.

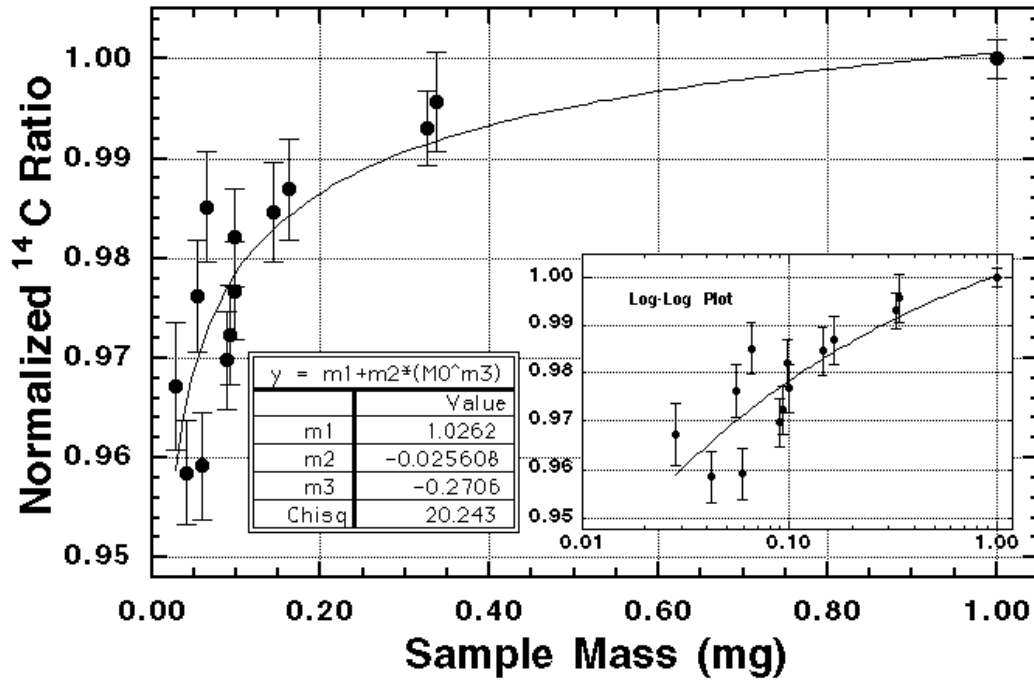


Figure 1: Normalized ratios obtained for Oxalic Acid Standard samples. The error bars are derived from counting statistics uncertainties in the $^{14}\text{C}/^{13}\text{C}$ ratios obtained for each sample and the 1 mg OX1 samples to which that sample was normalized. The black line shows the error-weighted curve that was fit to the data; the values of the constants obtained from this fit are shown (inset box). For clarity, the data are also shown on a log-log plot (inset plot).

The normalized ratios obtained for the “ ^{14}C -free” background samples are shown in Figure 2. The increase in the normalized ratios with decreasing sample mass can be attributed to the addition of contaminant carbon with a non-zero ^{14}C content. Several “ ^{14}C -free” background materials were used in obtaining these data: 1) Coal (supplied by Beta Analytic), 2) Calcite (TIRI sample F: Icelandic doublespar), 3) QL4766 wood (>56.6 ka BP), 4) QL1428 wood (>55 ka BP), and 5) Yale Anthracite (YA-13; no measurable ^{14}C activity). The latter three samples, and their ^{14}C contents, were provided by the Quaternary Isotope Laboratory, University of Washington (Stuiver, pers. comm., 1996). In our measurements there were no significant differences between the results obtained for these background materials, and the data from all of these materials were used.

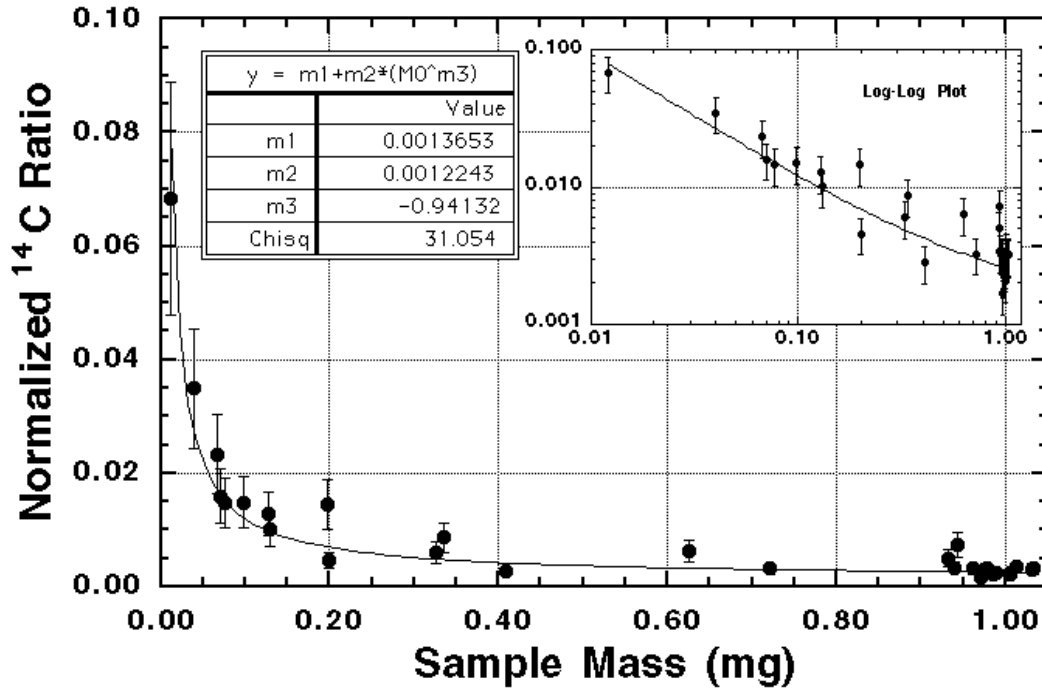


Figure 2: Normalized ratios obtained for Background (“ ^{14}C free”) samples. The error bars are derived as for the data in Figure 1. The black line shows the error-weighted curve that was fit to the data; the values of the constants obtained from this fit are shown (inset box). For clarity, the data are also shown on a log-log plot (inset plot).

The mass and ^{14}C content of the contaminant were determined from the OX1 and “ ^{14}C -free” background data using formulae derived previously [6, 7]:

1) the mass of the contaminant (m_c) was calculated from

$$\frac{m_c}{m_s + m_c} = 1 - \left(\frac{R_{OX1}^{(m_s)}}{R_{OX1(1mg)}} - \frac{R_b^{(m_s)}}{R_{OX1(1mg)}} \right)$$

where R = measured $^{14}\text{C}/^{13}\text{C}$ ratio; (m_s) indicates that the ratio is for sample s of mass m ; ($m_c + m_s$) = total mass of the sample (contaminant plus original sample); subscript c indicates the contaminant; subscript OX1 indicates an OX1 sample; subscript OX1(1 mg) indicates a 1 mg OX1 sample; and subscript b indicates a “ ^{14}C -free” background sample:

2) the ^{14}C content of the contaminant (R_C/R_{OX1}) was calculated from

$$\frac{R_C^A}{R_{\text{OX1}}^A} = \left[1 + \left(\frac{1 - \frac{R_{\text{OX1}}(m_s)}{R_{\text{OX1}}(1\text{mg})}}{\frac{R_b(m_s)}{R_{\text{OX1}}(1\text{mg})}} \right) \right]^{-1}$$

where, in addition to the previous definitions, superscript A indicates the actual value of a ratio rather than a measured value. For these calculations, the OX1 and “ ^{14}C -free” background data were fit with error-weighted curves of the form $y = a + bx^{-c}$, and values interpolated from these fits were used in equations (1) and (2) to calculate the mass and ^{14}C content of the contaminant for a set of representative sample masses ranging from 10 μg to ~ 1 mg. Nominal values for the contaminant mass and ^{14}C content of 2.6 μg and 0.42 times OX1, respectively, were obtained from these calculations.

However, examination of the OX1 and background data shows that the actual contaminant does not agree in detail with the “constant mass and ^{14}C content” model. In particular, the apparent leveling-off of the “ ^{14}C -free” background data for sample masses larger than ~ 0.75 mg suggests a low-level contribution from a sample-size-independent source; candidate sources for such contributions include residual carbon contamination in the ion source and intrinsic carbon in the Co catalyst used in graphitizing the samples. This dependence of contaminant mass and ^{14}C content on processed sample mass implies that background correction formulations that are strictly based on a “constant mass and ^{14}C content” contaminant may not provide accurate corrections in some cases.

Measurements of ANU Sucrose and “one-half-life old” test samples

In the second part of this study, the $^{14}\text{C}/^{13}\text{C}$ ratios of series of samples of ANU Sucrose and an ~one-half-life old material (QL11658; provided by M. Stuiver, QIL, UW) were measured. These series spanned the mass range 10 μg to ~1 mg and were measured under our routine measurement procedures, as described above. The normalized ratios obtained for the ANU Sucrose samples are shown in Figure 3.

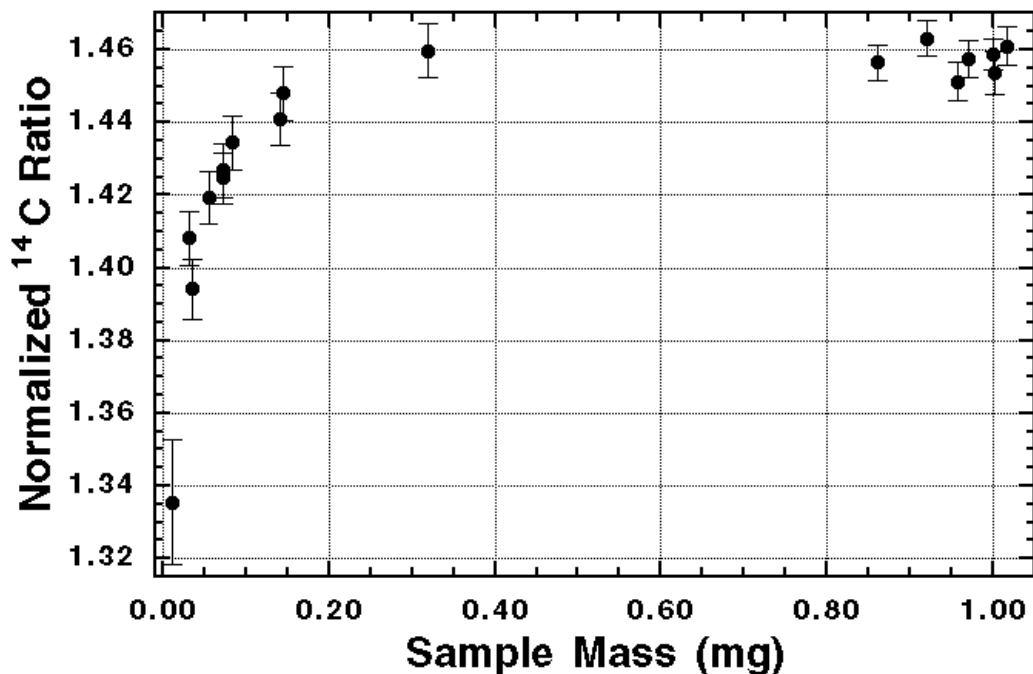


Figure 3: Normalized ratios obtained for ANU Sucrose samples. The error bars are derived as for the data in Figure 1.

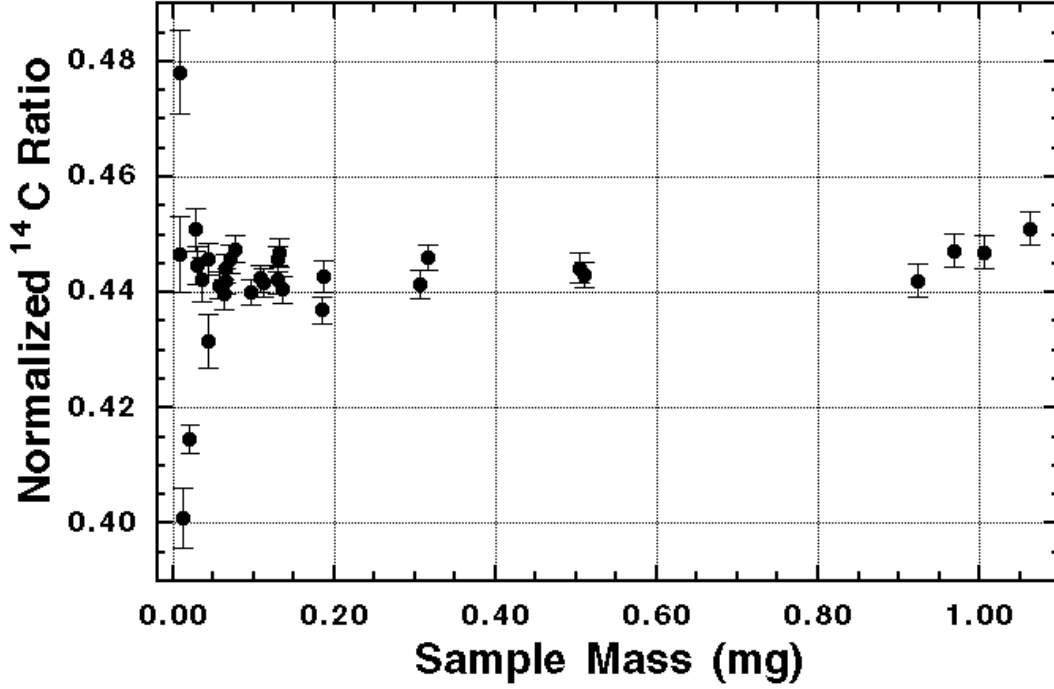


Figure 4: Normalized ratios obtained for QL11658 samples. The error bars are derived as for the data in Figure 1.

The normalized ratios obtained for the QL11658 samples are shown in Figure 4. The lack of a significant dependence of the normalized ratios on sample mass can be attributed to the contaminant carbon having essentially the same ¹⁴C content as the ~one-half-life old material; the nominal ¹⁴C content of the contaminant was 0.42 times OX1 and the measured values obtained for the QL11658 samples were ~0.44 times OX1. The much larger than expected scatter of the results for $\leq 25 \mu\text{g}$ samples suggests that, for reasons that are not understood, measurements on such ultrasmall samples are not reliable at present. All data for the QL11658 samples smaller than $25 \mu\text{g}$ have therefore been excluded from subsequent considerations.

Background Correction Calculations

The first of the three background correction formulations chosen for this study was published by Donahue *et al.* [5]. Their equation has a relatively simple form and is algebraically identical to Gillespie and Hedges' [4] formulation. We have adapted Donahue *et al.*'s equation for use in this study to yield:

$$\frac{R_S^A}{R_{OX1}^A} = \frac{R_{S^{(m_s)}}}{R_{OX1(1mg)}} \left(1 + \frac{R_{b^{(m_s)}}}{R_{OX1(1mg)}} \right) - \frac{R_{b^{(m_s)}}}{R_{OX1(1mg)}}$$

where the symbols follow the definitions given above. Donahue *et al.* derived this equation under the assumption that the ^{14}C content of the contaminant was equal to that of the standard. Donahue *et al.* also derived an expanded equation which did not require that assumption, but the simpler equation is more widely used, and hence, was used in this study.

The second formulation was based on a two-component mixing model in which contaminant carbon is mixed with the sample carbon for each processed unknown, standard, and blank sample [6, 7]. The equation derived under this model has the form:

$$\frac{R_s^A}{R_{OX1}^A} = \frac{R_s}{R_{OX1}} \frac{\left[1 - \left(\frac{h_{b_s}}{1 - h_{b_{OX1}}(C_{OX1}^{-1})} \right) \left(\frac{R_s}{R_{OX1}} \right)^{-1} \right] (1 - C_{OX1} h_{b_{OX1}})}{\left[1 - \left(\frac{h_{b_{OX1}}}{1 - h_{b_{OX1}}(C_{OX1}^{-1})} \right) \right] (1 - C_s h_{b_s})}$$

where h_{bx} is the ratio of the measured ratios obtained for a background (“ ^{14}C free”) material of mass x and a 1 mg OX1 sample, i.e., $R_b(m_x)/R_{OX1}(1 \text{ mg})$; C_x is the reciprocal of the contaminant ^{14}C content for a sample of mass x (obtained in preceding calculations), i.e., $(R_c(m_x)/R_{OX1}(1 \text{ mg}))^{-1}$; and the remaining symbols follow the definitions given above.

The last of the three background correction formulations chosen for this study was the traditional “subtraction ratio” formulation:

$$\frac{R_s^A}{R_{OX1}^A} = \frac{R_s(m_s) - R_b(m_s)}{R_{OX1}(m_s) - R_b(m_s)}$$

where the symbols follow the definitions given above. In the simulated sample tests mentioned above, this formulation provided accurate corrections for the contaminant only when the unknown sample, the OX1 standard and the blank sample were all of the same mass (m_s).

Background-corrected normalized ratios, R_s^A/R_{OX1}^A , were calculated for the ANU Sucrose and QL11658 data shown in Figures 3 and 4 using these three background correction equations. The values for OX1 and “ ^{14}C -free” background samples necessary for these calculations, e.g., $R_b(m_s)$, $R_{OX1}(m_s)$, $R_{OX1}(1 \text{ mg})$, etc., were

determined by interpolation of the error-weighted curves fit to the data in Figures 1 and 2. Estimated errors were assigned to the interpolated values based on the scatter of the OX1 and “ ^{14}C -free” background data about the fit curves and on individual measurement uncertainties. From these background-corrected normalized ratios, per cent Modern Carbon (pMC) values were calculated for the ANU Sucrose samples, and ^{14}C ages were calculated for the QL11658 samples.

Results and Discussion

The pMC values obtained for the ANU Sucrose samples are shown in Figure 5. Results obtained using Donahue *et al.*’s formulation show a distinct trend towards lower pMC values with decreasing sample mass. The pMC values calculated using the “two-component mixing” and the “subtraction-ratio” formulations are consistent, within uncertainties, with the consensus pMC value for ANU Sucrose of 150.61 ± 0.11 pMC [8].

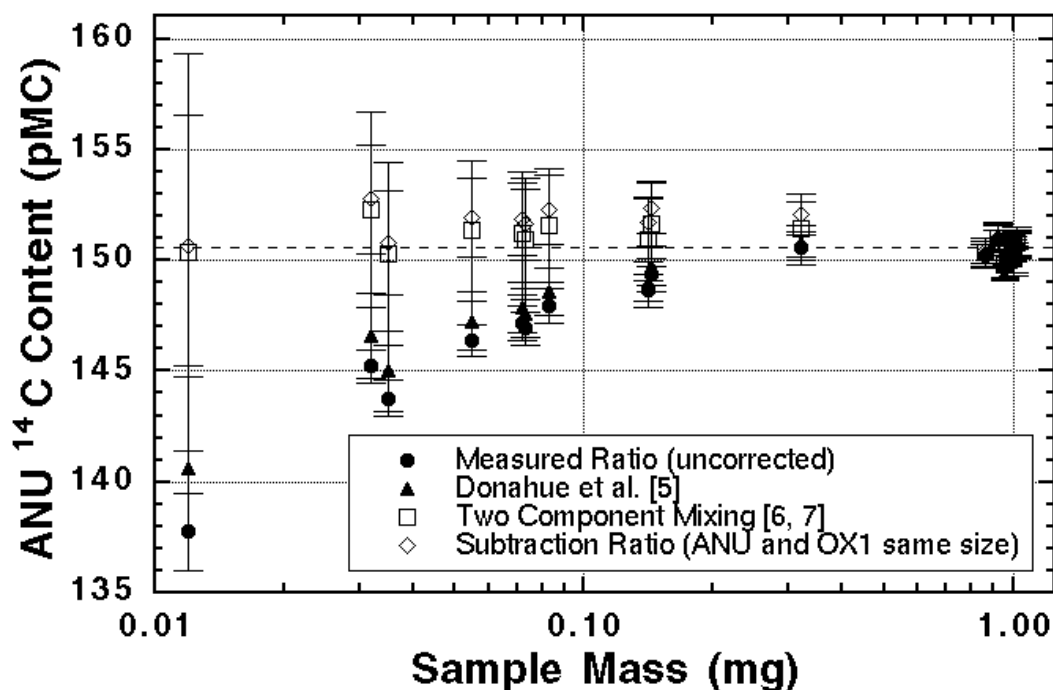


Figure 5: pMC values obtained for ANU Sucrose samples. The values were obtained using the following background correction formulations: 1) no correction (filled circles), 2) Donahue *et al.*’s [5] (filled triangles), 3) “two-component mixing” [6, 7] (open squares), and 4) “subtraction ratio” (open diamonds). Representative error bars for the first two of these sets are shown for several of the Donahue *et al.* values, and representative error bars for the final two sets (3 and 4) are shown for several of the “subtraction ratio” values. The dashed line shows the consensus pMC value for ANU Sucrose of 150.61 ± 0.11 [8].

The ^{14}C ages obtained for the QL11658 samples are shown in Figure 6. As would be expected, the ages derived directly from the measured ratios without background correction show no dependence on sample mass because the contaminant has essentially the same ^{14}C content as the samples. Results obtained for the QL11658 samples using Donahue *et al.*'s formulation again show a trend towards lower ^{14}C contents (older ages) with decreasing sample mass. The ^{14}C ages obtained using the “two-component mixing” and the “subtraction-ratio” formulations show no dependence on sample mass, and are consistent with previously obtained ^{14}C ages for QL11658 (6120 ± 30 BP [9] and 6140 ± 30 BP [6]).

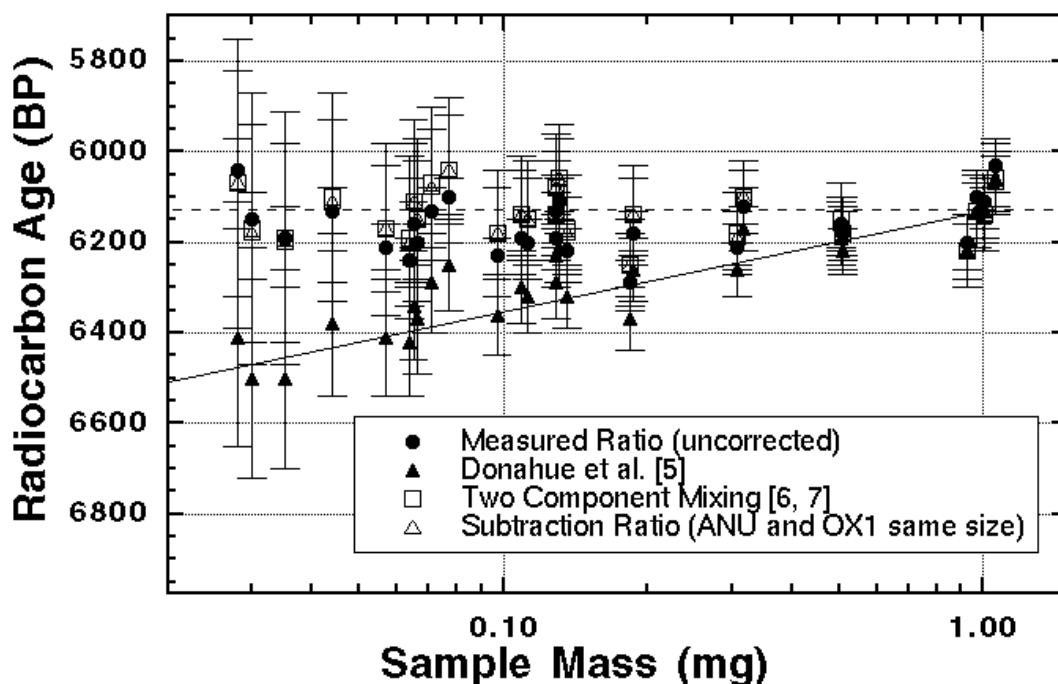


Figure 6: ^{14}C ages obtained for QL11658 samples. The ^{14}C ages were obtained using the same correction formulations as in Figure 5, and the error bars are representative of the uncertainties in the values as described for Figure 5. The dashed line shows the ^{14}C age of QL11658 from previous measurements [6, 9], and the black line shows the trend of the values obtained using Donahue *et al.*'s formulation.

The data obtained using Donahue *et al.*'s formulation for both the ANU Sucrose and the QL11658 samples demonstrate that this equation does not provide accurate corrections for the contaminant's contribution to $^{14}\text{C}/^{13}\text{C}$ ratios obtained for small samples. In qualitative terms, this is because Donahue *et al.*'s formulation does not accurately account for the proportionately larger amount of “extra” ^{13}C that the 0.4-OX1 contaminant added to the small ANU Sucrose samples relative to the ^{13}C the contaminant added to the large OX1 standard samples.

Conclusions

Through measurements of $^{14}\text{C}/^{13}\text{C}$ ratios of OX1 and ^{14}C “dead” materials which spanned the mass range from 10 μg to ~ 1 mg, nominal values for the mass and ^{14}C content of the contaminant carbon introduced during sample processing in our laboratory of 2.6 μg and 0.42 times OX1, respectively, were obtained. Measured $^{14}\text{C}/^{13}\text{C}$ ratios from ANU Sucrose and “ \sim one-half-life old” test samples, which spanned the same mass range, showed sample-mass-dependent variations that were consistent with that contaminant. The application of three background correction formulations to the ANU Sucrose and the “ \sim one-half-life old” data showed that: 1) the “two-component mixing” formulation provided accurate background corrections when $^{14}\text{C}/^{13}\text{C}$ ratios obtained for small unknown samples were normalized to ratios obtained for large standard samples, 2) the “subtraction-ratio” formulation provided accurate corrections when all of the $^{14}\text{C}/^{13}\text{C}$ ratios (unknown, standard, and background) were obtained from samples of the same mass, and 3) Donahue *et al.*’s formulation did not provide accurate corrections for small samples when the masses of the unknown and standard samples differed, and the ^{14}C content of the contaminant differed from that of OX1 and/or the test samples. These experimental results are in agreement with the results of previous sample simulation tests [6, 7].

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